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A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
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The Magnetic Susceptibilities of Metals Dissolved in Liquid Ammonia

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(Received April 30, 1943)

Here are recorded data on the magnetic susceptibilities of potassium and of cesium dissolved in liquid ammonia at 240°K and 220°K. Also included are a few data on calcium and barium. These solutions throughout the entire range of concentrations were regarded as representing an electron gas. Such systems would permit the distributions of the magnetic moments of the electrons to be followed continuously from the degenerate region of the Fermi-Dirac statistics to those distributions where the quantum and classical statistics are indistinguishable. The general features of the magnetic behavior of a free electron gas

were recognized, overlaid, however, by interactions characteristic of the environment of the electrons in the solutions. In the light of the magnetic susceptibilities as well as of other properties, a description is proposed for the structure of the solutions with special reference to the conduction electrons. Barium was found to dissociate into two electrons per gram atom and it is inferred that calcium dissociated likewise, but much greater dilutions would be required for a satisfactory demonstration. A method of considerable sensitivity and accuracy has been developed for measuring the magnetic susceptibilities of substances at low temperatures.

METALS dissolved in liquid ammonia have the property, primary for the present investigation, of dissociating into electrons and positive metal ions.¹

In dilute solution, the conduction is electrolytic with the electrons as the negative ions carrying

most of the current. The conductivity changes continuously with concentration and becomes metallic in the strong solutions. When saturated, a solution of sodium possesses about twice the conductivity of mercury at room temperature. Along with this behavior go changes in color which is a pale transparent blue in great dilution, deepens into a dense dark blue when more metal is dissolved, and acquires in concentrated solu-

¹ This classical work of Kraus is summarized by him in J. Frank. Inst. 212, 537 (1931). Also in C. A. Kraus, *The Properties of Electrically Conducting Systems* (Chemical Catalog Company, New York, 1922).

tions a metallic bronze-like luster giving the solution every appearance of being a liquid metal. When the solvent is evaporated, the original metal is regained. In the case of lithium and also of calcium the metallic crystals which first deposit from the solution contain ammonia bound stoichiometrically, $\text{Li}(\text{NH}_3)_4$ and $\text{Ca}(\text{NH}_3)_6$. The former even at low temperatures dissociates into ammonia gas and the metal powder.

These phenomena speak strongly for regarding the solutions as a liquid metal whose concentration can be varied continuously over a great range. Like metals, the solutions may presumably be conceived as an electron gas which in better approximation is to be counted as subject to the microscopic fields in the solution.

The magnetic measurements were undertaken in order to follow the distribution in spin or magnetic moment among the electrons as a function of concentration and temperature. At high electron concentration, we would expect according to Pauli's well-known work² almost all the electrons to have paired-off their spins, the degenerate state of the Fermi-Dirac statistics, whereas in very dilute solutions, the elementary magnets would be independent of each other and conform to those distributions of the Fermi-Dirac statistics which are indistinguishable from the distributions of the classical statistics. To achieve a comparable variation in spin with the high electron densities prevailing in metals, it would be necessary according to theory to raise the temperature above the so-called degeneracy temperature, the order of 20,000°. By diluting the electrons of the metal, in our experiments with liquid ammonia, the degeneracy temperature would be greatly reduced, even considerably below the temperature where magnetic measurements are possible.

The degeneracy temperature is given by

$$T_0 = \frac{h^2}{2mk} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}},$$

where h is Planck's constant, m is the mass of the electron, k is Boltzmann's constant, N is the number of electrons in the volume V .

In a previous work,³ it was shown that in its general features, the course of the variation of the susceptibilities was consistent with this outline. When sodium was at a concentration 0.5M, its atomic susceptibility was of the same order of magnitude as that of the bulk metal. The degeneracy temperature for this concentration was about 2000°K, ten times higher than the temperature of the substance 230°K and, hence, the electrons were degenerately distributed. At

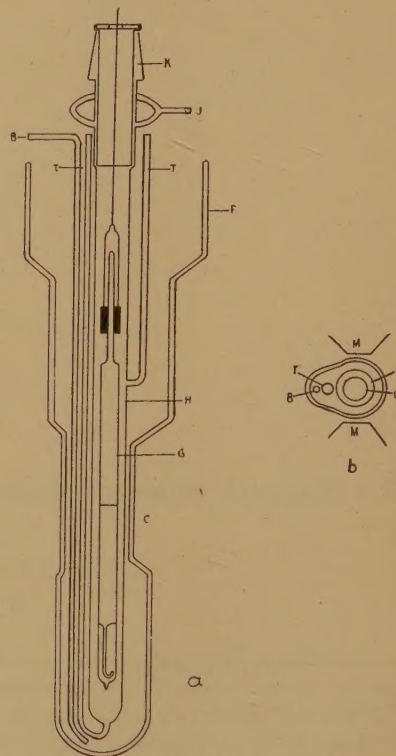


FIG. 1. Apparatus for measuring magnetic susceptibilities of substances at low temperature.

0.002M with the degeneracy temperature at about 50°K, the atomic susceptibility had increased about one hundred fold and had attained values expected of an electron gas according to classical statistics.

These results were confirmed in the more extensive investigation of Huster and Vogt.^{4,5} However, the data lacked the precision required for interpretation, especially in very dilute solutions where the actual forces to be measured were

³ S. Freed and H. G. Thode, *Nature* **134**, 774 (1934).

⁴ E. Huster and E. Vogt, *Physik. Zeits.* **38**, 1004 (1937).

⁵ E. Huster, *Ann. d. Physik* **33**, 477 (1938).

² W. Pauli, *Zeits. f. Physik* **41**, 81 (1927).

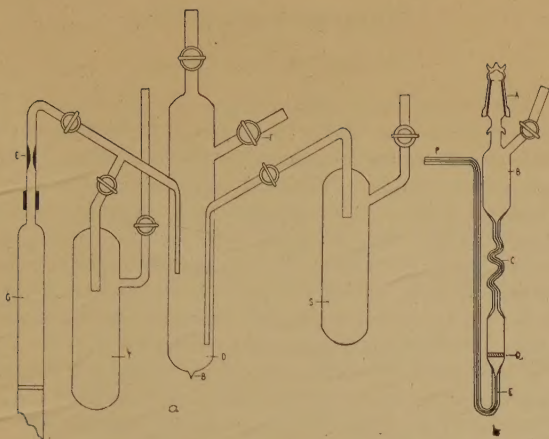


FIG. 2. Apparatus for preparing solutions of metals in liquid ammonia.

extremely small. Since the atomic susceptibility of sodium proved to have less than the theoretical value, the measurements had to be pushed to extreme dilutions in order to discover the limiting susceptibility. For this reason, we turned to solutions of potassium whose electrons would supposedly be "freer" than those of sodium; the conductivities at the same concentrations were known to be consistently higher. The susceptibilities were actually found greater and a satisfactory precision was obtained in the measurements. Also included in this communication are susceptibilities of solutions of cesium, of barium, and of calcium.

EXPERIMENTAL

Apparatus

A refinement⁶ of the Gouy method of measuring magnetic susceptibilities was made available for substances at low temperatures without appreciable decrease in accuracy.

A vertical tube divided into equal sections by a horizontal partition is suspended from the arm of a microbalance so that the partition comes into the center of the pole gap of a magnet. One-half of the tube is filled with the solution and the other with the pure solvent. Under these conditions the susceptibility of the dissolved substance per unit volume in dilute solution is given directly by

$$K = K_{\text{solution}} - K_{\text{solvent}} = \frac{2F}{A(H_1^2 - H_2^2)},$$

⁶ S. Freed and C. Kasper, Phys. Rev. **36**, 1002 (1930).

where K is the specific volume susceptibility of the solution minus that of the solvent, F is the vertical force exerted on the balance arm, A is the cross-sectional area of the tube, H_1 is the field strength at the partition, while H_2 is that at the ends of the tube. In the more concentrated solutions, account must be taken of the fact that the solvent material in unit volume of the solution is not identical in amount with that in unit volume of pure solvent. This correction is usually small and altogether negligible in the more dilute solutions.

To extend the usefulness of this procedure for substances at low temperatures, the method consisted in suspending the glass tube G (Fig. 1a) in an atmosphere of stagnant hydrogen inside a tube H which was kept at the low temperature by the surrounding refrigerant liquid. A stream of dry hydrogen entered the stationary tube H at the upper end J and flowed to the outside atmosphere at such a rate as to keep the air with its moisture from descending during the experiment and affecting the weight of the tube G . Baffles with small openings could be mounted horizontally on the ends of the tube K which was perforated to allow easy entry of the hydrogen from the tubes J . The refrigerant, liquid ammonia, was kept in the Dewar vessel F . Its cap, not shown, was provided with connections to a manometer and pump for reducing the pressure and consequently the temperature of the refrigerant. The tubes T , T contained single junction thermocouples which abutted into H . The temperatures at the different levels of the hydrogen atmosphere as read by the thermocouples rarely varied by more than one-half degree even under unfavorable conditions. B was a capillary tube for the passage of air into the liquid ammonia to lessen the bumping of the liquid while it was being pumped.

The Dewar vessel F had a circular cross section with exception of the region C (Fig. 1b). This fitted into the pole gap and was therefore designed to separate the pole pieces as little as possible and yet accommodate the tubes T and B . The cylindrical tubing had been here enlarged on one side by means of a carbon form pressing out the glass while it was heated and softened without affecting the diameter of the circular portion.

G contained a trap at the lower end as shown

(Fig. 1a). By this means the bubble of ammonia gas occupying the space left between the liquid and seal would not rise to the partition when the tube was inverted to its normal position for weighing. The liquid in *G* extended, then, in an unbroken column except for the horizontal glass partition.

Calibration and Measurement

The Gouy method for determining susceptibilities requires three measurements of force, a blank run on the container, a calibration with a substance whose absolute susceptibility is known, and finally the measurement of the material of interest.

Both portions of *G* were filled with liquid ammonia for the blank run. Ideally under these conditions the force would be zero but since the system was not perfectly symmetrical small correction forces were to be expected. The dissymmetry due to the temperature gradient was so small that it was ignored. The extreme variation in the forces was as a rule not more than ± 0.003 mg from day to day. Pure liquid ammonia served for the calibration. Its susceptibility had been determined within an accuracy of one to two percent by Huster. The relative susceptibilities of the solute as measured by the present method were practically independent of the value accepted for the susceptibility of liquid ammonia. The absolute value was, however, determined by it.

For the calibration, the upper part of the tube *G* was filled with liquid ammonia, the lower portion was left evacuated and the net force noted on the balance at definite field strengths, i.e., definite currents in the electromagnet. The computations were made here as well as in all the measurements at 15.0 amp. with the corresponding field at about 15,000 gauss. The value at 15.0 was taken from a graph of forces against current. Although the individual points, in the measurements of the solutions, differed from the average by as much as 0.005 mg, it was found that in a twenty-four hour period, this average did not change by more than ± 0.002 mg. This variation together with that of the blank produced a probable error of ± 0.005 mg in the net force.

The tube factor defined as the ratio of the susceptibility to force changed less than 1 percent over the temperature range -33°C to -53°C .

At lower temperatures, the weighings were somewhat less accurate. When the bath was pumped to obtain lower temperatures, the ammonia bumped. This was almost entirely eliminated by aspirating air through the capillary tube *B*. To obtain a uniform temperature throughout the refrigerating liquid it was found necessary to heat the bath slightly throughout its length, a function performed with bare platinum resistance wire. In this manner, the temperature of the bath could be controlled to better than a degree with a temperature difference of less than one-half degree between the top and bottom.

Preparation of Solutions

Potassium and Cesium

The solutions were prepared in an all glass vacuum line system adapted by H. G. Thode and R. P. Metcalf of this laboratory from the procedures developed by Kraus and by Gibson and Phipps.⁷ The metal was introduced into *D* at the point *B* (Fig. 2a) by distillation. A length of capillary had been filled with the metal and a section of the appropriate length was broken off for each concentration. The desired amount, within ten percent, was slowly distilled into *D* by the use of free flame. Ammonia which had been twice dried over potassium was condensed into *D*. The condensation was complete after there was enough solution in *D* above the upper siphon so that *G* could be filled and an aliquot portion of the remainder could be siphoned into *T*. The solution was then stirred by creating a slight vacuum and so bringing about vigorous boiling. The solution was then successively siphoned into *G*, *T*, and *S*. *G* was sealed off at *E* and the solutions in *T*, *S*, and *D* were kept for analysis.

Calcium and Barium

Because of the high melting points of these metals, another method was devised for introducing them into *D*.

TABLE I. Susceptibilities per gramatom χ_A .

Moles liter	Force (corrected) (mg)	$K \text{ soln} - K_{\text{NH}_3}$ $\times 10^6$	$\chi_A \times 10^6$	Free electron gas $\chi_A \times 10^6$
Potassium 240°K				
0.00341	0.123	0.00432	1268	1530
0.00384	0.127	0.00452	1180	1525
0.00406	0.152	0.00505	1240	1522
0.00481	0.160	0.00570	1180	1520
0.00812	0.222	0.00790	974	1505
0.00960	0.246	0.00819	853	1480
0.0318	0.359	0.01280	402	1060
0.482	1.126	0.0390	29.9	310
Potassium 220°K				
0.00354	0.078	0.00286	809	1630
0.00422	0.100	0.00332	790	1620
0.00501	0.118	0.00417	834	1600
0.00844	0.116	0.00411	488	1550
0.0331	0.213	0.00765	232	1220
0.500	0.558	0.0194	-7.7	310
Cesium 240°K				
0.00415	0.139	0.00470	1130	1500
0.00582	0.214	0.00724	1245	1480
0.00690	0.207	0.00700	1013	1460
Cesium 220°K				
0.00432	0.096	0.00325	755	1620
0.00605	0.183	0.00618	1020	1580
0.00718	0.139	0.00472	657	1560
Calcium 240°K				
0.00244	0.077	0.00274	1140	3060
0.0100	0.145	0.00531	938	2840
Calcium 220°K				
0.00255	0.069	0.00245	978	3300
0.0105	0.079	0.00283	271	3040
Barium 240°K				
0.00106	0.066	0.00235	2280	3400

⁷ G. E. Gibson and T. E. Phipps, J. Am. Chem. Soc. **48**, 312 (1926).

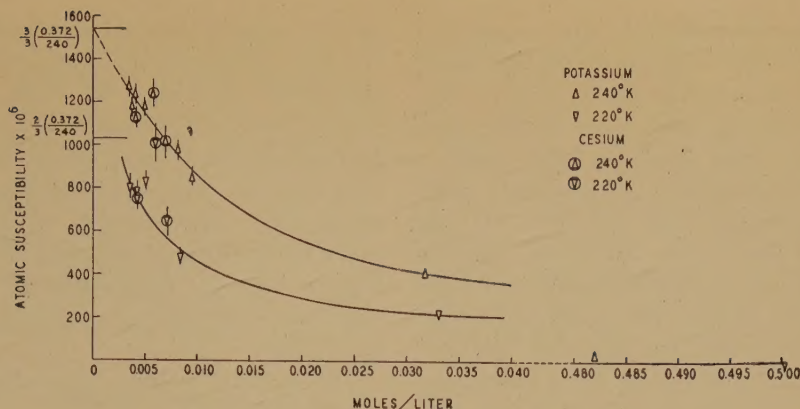


FIG. 3. Atomic magnetic susceptibility as a function of concentration.

The apparatus represented in Fig. 2b was sealed onto the vacuum line; *F* was joined to *F* on *D* (Fig. 2a). After the system had been thoroughly pumped, flamed, and flushed with gaseous and liquid ammonia, a piece of the metal was put into *B* and the system highly evacuated. Ammonia was then condensed on the metal so that the saturated solution which formed ran down the spiral capillary tubing *C* and through the filter plate *D*, a 01 Selas clay filter. This solution was siphoned into *D* through the stopcock *F*.

Analyses of Concentrations

The volumes of the solutions contained in traps *S*, *D*, and *T* were determined by distilling the ammonia into three measuring cells of the type described by Kraus.⁸ After the ammonia had been distilled from *S*, *D*, and *T*, the residue was dissolved in water, boiled to remove ammonia and titrated with 0.01*N* HCl. The concentrations of the solutions in *D* were usually about 5 percent higher than those in *T* and *S* which agreed with each other within better than 1 percent. The higher concentration in *D* was doubtless due almost entirely to some undissolved metal which had condensed during the distillation considerably above the solution line. Because of good agreement in the analyses of the solutions in *T* and *S* and because siphonings were rapid, the concentration was taken as the average in *T* and *S*. In a few instances, *D* was averaged in if some mishap occurred to one of the other.

Previous work⁹⁻¹¹ has shown that the densities of the dilute solutions were practically identical with that of pure ammonia. Only in the most concentrated solution of potassium is the difference appreciable and the correction was applied. The actual density was obtained by interpolation from the data of Johnson and Meyer.

The experimental errors were incurred almost solely through the errors in weighing; the errors in analyses were relatively small.

⁸ C. A. Kraus, J. Am. Chem. Soc. **43**, 749 (1921).

⁹ C. A. Kraus, E. S. Carney, and W. C. Johnson, J. Am. Chem. Soc. **49**, 2206 (1927).

¹⁰ W. C. Johnson and A. W. Meyer, J. Am. Chem. Soc. **54**, 3621 (1932).

¹¹ E. Huster, Ann. d. Physik **33**, 477 (1938).

The errors in the analyses of potassium and of cesium amounted to less than 1 percent, in calcium 2 percent, in barium 3.5 percent.

EXPERIMENTAL RESULTS AND DISCUSSION OF DATA

The data for the four metals measured are gathered in Table I and are also presented in the graph (Fig. 3).

The following features of the data support the idea held at the beginning that the solutions may be taken to represent an electron gas.

(1). In great dilution, the atomic susceptibility approximates the value which would arise from independent elementary magnets possessing one-half unit of spin.

(2). The concentrated solutions which obviously possess strongly metallic properties furnish atomic susceptibilities in rough agreement with the presence of an electron gas free to move throughout the volume. For example, Huster found that a saturated solution of sodium had an atomic susceptibility of about 80×10^{-6} whereas a free electron gas in the same volume would have about 40×10^{-6} .

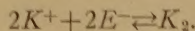
(3). With increase in atomic volume, the atomic susceptibility increased. At 240°, the concentration where the steep increase sets in occurred at about 0.01*M*. The ideal theory has 0.02*M* as the concentration where the degenerate gas begins to pass into the classical distributions at 240°K. With increasing temperature, Fig. 3 indicates, the difference between the corresponding concentrations diminishes.

It is evident that the model of a free electron

gas must be extended to include interaction with the environment. Free electrons would because of their motion in a magnetic field show a diamagnetism¹² cancelling one third of the spin magnetism. The data establish that such a cancellation does not occur; the two-third value of the spin paramagnetism indicated by the lower horizontal line on the left of the graph is exceeded and the susceptibilities continue toward the full value due to spin, the upper horizontal line. Peierls¹³ has raised the question whether Landau's conclusions are valid for a condensed system where the average frequency of collisions between the electrons and their environment is high.

The actual susceptibilities are in general lower than computed¹⁴ for a free electron gas (last column of Table I) and even more drastic departure from such a model comes to light in the temperature dependence of the susceptibilities which decrease rather than increase with decreasing temperature.

To account for such a behavior, the idea naturally suggests itself that electrons are removed by the positive ions to form diamagnetic potassium molecules



It should be noted that the formation of potassium atoms or of molecular ions would instead increase the susceptibilities. Huster had assumed the presence of diatomic molecules in solutions of sodium. A computation shows, however, that the concentration of the molecules needed for agreement with the susceptibilities appears in conflict with the molecular weight of dissolved sodium as revealed by Kraus¹⁵ measurements of vapor pressures. There are other factors too which indicate that the hypothesis of dissolved diatomic molecules is rather forced. The very dilute solutions and the very concentrated solutions both are in agreement with a system consisting only of electrons and separate ions. The existence of the metals such as $\text{Li}(\text{NH}_3)_4$, $\text{Ca}(\text{NH}_3)_6$, $\text{Sr}(\text{NH}_3)_6$, $\text{Ba}(\text{NH}_3)_6$ containing the same number of ammonia molecules as completely surround the

positive ions in their salts indicates strongly that the ions are separated from each other in these metals by ammonia. We shall take the single point of view that throughout the entire range of concentrations all these solutions consist of positive ions and electrons in ammonia and that no appreciable concentration of diatomic linkage exists between metal atoms or ions. We shall then inquire into the disposition of the conduction electrons to which the lower susceptibilities may be ascribed.

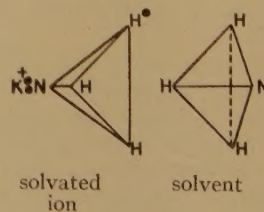
The specific volume susceptibility of a degenerate gas is given by^{16,17}

$$K = 2\mu^2(dZ/dE)_{E=E_0},$$

where K is the susceptibility per unit volume, μ is the Bohr magneton, and $(dZ/dE)_{E=E_0}$ is the number of energy levels per unit energy range at the top of the Fermi distribution. The energy of interaction of the magnetic moments of the electrons with the external field serves to uncouple the pairs of electrons in the filled cells and send some into empty ones so that the spins are in line. The effectiveness of this process depends upon the number of cells (or levels) which are available to the energy of interaction. Therefore, the more widely separate are the levels, the lower is the susceptibility.

It has been shown by Bardeen¹⁸ that when resonance energies are included the resulting decrease in the density of levels lowers the magnitude otherwise computed for the heat capacity of metals. Magnetic susceptibilities are affected in the same general way.

This resonance binding may, we propose, be represented as follows:



where the ammonia near the K^+ corresponds to

¹² L. Landau, *Zeits. f. Physik* **64**, 629 (1930).

¹³ R. Peierls, *Zeits. f. Physik* **80**, 763 (1933).

¹⁴ N. F. Mott, *Proc. Camb. Phil. Soc.* **32**, 108 (1936).

¹⁵ C. A. Kraus, *J. Am. Chem. Soc.* **30**, 1197 (1908).

¹⁶ W. Pauli, *Zeits. f. Physik* **41**, 81 (1927).

¹⁷ W. F. Mott and H. Jones, *Theory of Properties of Metals and Alloys* (The Clarendon Press, Oxford, 1936), p. 184.

¹⁸ J. Bardeen, *Phys. Rev.* **50**, 1098 (1936). See, e.g., F. Seitz, *Modern Theory of Solids* (New York, McGraw-Hill, 1940), p. 421.

one of the molecules of solvation and the ammonia structure facing it represents the solvent, in general, but may also on occasion stand for ammonia of solvation of another potassium ion. Structures with the electron near one of the hydrogen atoms may be imagined stabilized by the many equivalent or nearly equivalent structures which the situation may assume. The mobility of the electron in electrolysis may be viewed as the passage of the electron from one hydrogen atom to another with some differentiation between the ammonia molecules of solvation and of solvent.

Also contributing to the decrease in susceptibility and especially to its decrease with the temperature is the interaction of pairs of electrons which have some resemblance to F' centers known in systems composed of a metal such as potassium dissolved in a crystal as potassium chloride. In a site where a negative ion is missing, two electrons can lodge with some stability.¹⁹ This pair is probably diamagnetic. In addition to the interaction having analogy with F' centers, the electron pairs are further stabilized through resonance in the same way as the unpaired electrons.

In our present schematization another electron would be attached, let us say, to one of the hydrogen atoms on the ammonia molecule to the right. The interaction of these electrons to form a diamagnetic pair would then account for the decrease in paramagnetism. Here again the electrical conductivity would be ascribed to the quantum mechanical passage through barriers somewhat as Farkas²⁰ assumed in an over-

simplified model. In this way there appears no contradiction with the molecular weights as derived from vapor pressure measurements.

With further increase in electron concentration, the increased interaction may be viewed as an increase in the Fermi zero-point energy which operates to oppose the local trapping within barriers. Such a process is consistent with the gentle increase in susceptibilities at still higher concentrations which Huster found.

The lower susceptibilities of sodium compared with potassium (or of calcium compared with barium) may be linked chiefly to the relative sizes of these ions. The smaller ion induces a greater polarization in the ammonia of solvation with more positive charge localized on the hydrogen atoms. Relative to these hydrogen atoms, the exchange energies are increased with consequent decrease in the density of energy levels. Associated with this influence lowering the susceptibilities there is another aspect—the deepening of the energy barriers would favor an increased stability and concentration of the electron pairs.*

The fact that the atomic susceptibility of barium is definitely greater than that arising from one electron per gram atom is sufficient evidence that the ion dissociates into two electrons per gram atom which interact of course, with their environment. It appears highly probable that calcium dissociates in the same way but, as would be expected, the interaction is greater.

*In a structureless medium, one expects on purely electrostatic grounds that the pairing of electrons would also take place to a greater degree with smaller ions. The Debye-Hückel ion atmosphere is here replaced by the electron atmosphere and with increased electrostatic potential from the smaller ion, there would be a greater probability of having more than one electron at a given distance from the center of this ion.

¹⁹ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, 1940), p. 128.

²⁰ L. Farkas, *Zeits. f. physik. Chemie* **A161**, 355 (1932).

